J Appl Electrochem (2014) 44:821–830
DOI 10.1007/s10800-014-0689-8

RESEARCH ARTICLE

Determination of lisinopril using β-cyclodextrin/graphene oxide-SO_3H modified glassy carbon electrode

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Received: 26 November 2013 / Accepted: 30 March 2014 / Published online: 17 April 2014

Abstract An electrochemical method has been successfully demonstrated for sensitive determination of lisinopril with β-cyclodextrin-graphene oxide-SO_3H composite modified glassy carbon electrode (β-CD/GO-SO_3H/GCE). Cyclic voltammetry, differential pulse voltammetry, and chronocoulometry were used to investigate the electrochemical behavior of lisinopril at β-CD/GO-SO_3H/GCE. The cyclic voltammetric results indicate that β-CD/GO-SO_3H/GCE can remarkably enhance electroactivity toward the oxidation of lisinopril in buffer solutions. The electrochemical behavior was further exploited as a sensitive detection scheme for the lisinopril determination by differential-pulse voltammetry. Under optimized conditions, the concentration range and detection limit were 0.21–190.4 and 0.11 μM (S/N = 3), respectively. The method was successfully applied to assay the drug in human serum.

Keywords Graphene oxide · Cyclodextrin · Lisinopril · Electrochemical sensor · Nanotechnology

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1 Introduction

Lisinopril, an inhibitor of the angiotensin converting enzyme (ACE), is widely used for treating high blood pressure and heart failure [1]. The measurement of this drug in biological fluids is challenging, since it has poor electromagnetic absorbance due to weak benzene chromophore [2]. A variety of analytical methods have been developed for the determination of lisinopril in pharmaceutical preparations, such as LC/MS [2], spectrophotometry and spectroflurimertric [3, 4], micellar electrokinetic chromatography [5], and ion-exclusion chromatography [6].

Methods have been described for determination of lisinopril in biological fluids including GC [7], HPLC [8–10], LC/MS [11], fluoroimmunoassay [12], radioimmunoassay [13], fluoro enzymatic assay [14], UV [15], and ion selective electrodes [16]. Although these methods have the advantages of sensitivity and accuracy, their high cost and complicated operation limit their extensive applications. The electrochemical methods, with respect to their sensitivity, accuracy, simplicity, and ease of on-site determination, have received considerable attention for the analysis of drugs [17–19].

Cyclodextrins (CDs) and their derivatives attracted more attention in the pharmaceutical field for the past few years and an increased number of reviews have been dedicated to their pharmaceutical applications [20–29]. CDs and their derivatives have well-known effects on drug solubility and dissolution, bioavailability, safety, and stability, and their applications in different areas of drug delivery have also been reported [28]. However, the cavity size of α-CD is insufficient for many drugs and ω-CD is expensive. Among CDs, β-CD is receiving increasing attention due to its low cost and cavity size suitable for the widest range of drugs in aqueous media.

CDs are a well-known class of natural host molecules obtained from the enzymatic degradation of starch [30–34]. CDs with their largely hydrophobic cavities of variable size and numerous ways of chemical modification are the subject of intensive electrochemical research including both their behavior in homogeneous solutions and in thin films attached to the electrode surfaces [35–37]. Electroanalytical methods measuring the current response to the potential applied, linear scan, staircase, pulse voltammetries, and potential-step techniques, such as chronoamperometry and chronocoulometry, allow to trigger or to monitor changes in the redox states of electroactive drugs entrapped on the sites in CD-based systems. Linear scan or staircase cyclic voltammetries (CV) are the most frequently employed electrochemical techniques for these studies. They provide useful information on the nature of the reduced and oxidized forms of the electroactive compounds such as drugs, and on the mechanistic aspects of the electrode processes. They also allow monitoring even very subtle changes of the molecular environment of the redox centers by following their redox potentials. Therefore, CDs are employed in electrochemical sensing devices for the determination of selected analytes.

One of the most important characteristics of CDs is the formation of inclusion complexes with various organic and inorganic guest molecules [38–41]. Upon inclusion complexation, the characteristic properties of the guest molecule inside the CD cavities, such as solubility, redox, and spectral will be changed significantly. This unique property has led to widespread utilization of CDs in pharmaceutical, chemical, and other industrial areas. The stability of the inclusion complexes depends on the size and the polarity of the guest molecules, the nature of the medium, and the temperature. Based on size selective complexation properties of CDs, the better the fit of guest molecules inside the cavity of CD, the more stable the complex will be produced. The stability of the complex is proportional to the polarity of the guest molecule. Lisinopril is a polar drug, therefore, entraping of this drug on CD can be surveyed. Lisinopril is an electroactive substance. However, its electrochemical signal cannot notably enhance when lisinopril molecule entered into the film containing β-CD at the β-CD-modified electrodes. The signal enhancement can be done by secondary materials such as multiwall carbon nanotubes (MWCNTs) [42], graphene [43], and so on. Compared with β-CD/MWCNTs-modified electrode, β-CD/graphene hybrid films showed most attractive analytical performance, as clearly illustrated from the response signal [42, 43].

These improved performances encouraged us to explore the possible leading role played by the presence of β-CD/graphene or its conductive derivatives such as graphene oxide (GO) and functionalized-graphene oxides. The large surface area of β-CD/GO-SO_3H can be provided by the three-dimensional structure of the deposited films and greatly increases Faradic currents. Therefore, in the present work, we used β-CD/GO-SO_3H as modifier material and studied the electrochemical oxidation of lisinopril at β-CD/GO-SO_3H-modified glassy carbon electrode and developing a new electroanalytical procedure for quantification of lisinopril in human serum samples. To the best of our knowledge, this is the first report of the determination of lisinopril based on its direct electrochemical oxidation on graphene or its derivatives.

2 Experimental

2.1 Chemical and reagents

All chemicals used in this work were of analytical reagent grade, from Merck (Germany). Lisinopril was kindly gifted by Sobhan Darou Co., (Rasht, Iran). The standard solution of authentic lisinopril was prepared by dissolving an accurate mass of the bulk drug in an appropriate volume of 0.1 M phosphate buffer solution (PBS), pH 6.00 (which was also used as supporting electrolyte), and then stored in the dark place at 4 °C. Additional dilute solutions were prepared daily by accurate dilution just before use. Lisinopril solutions were stable and their concentrations did not change with time.

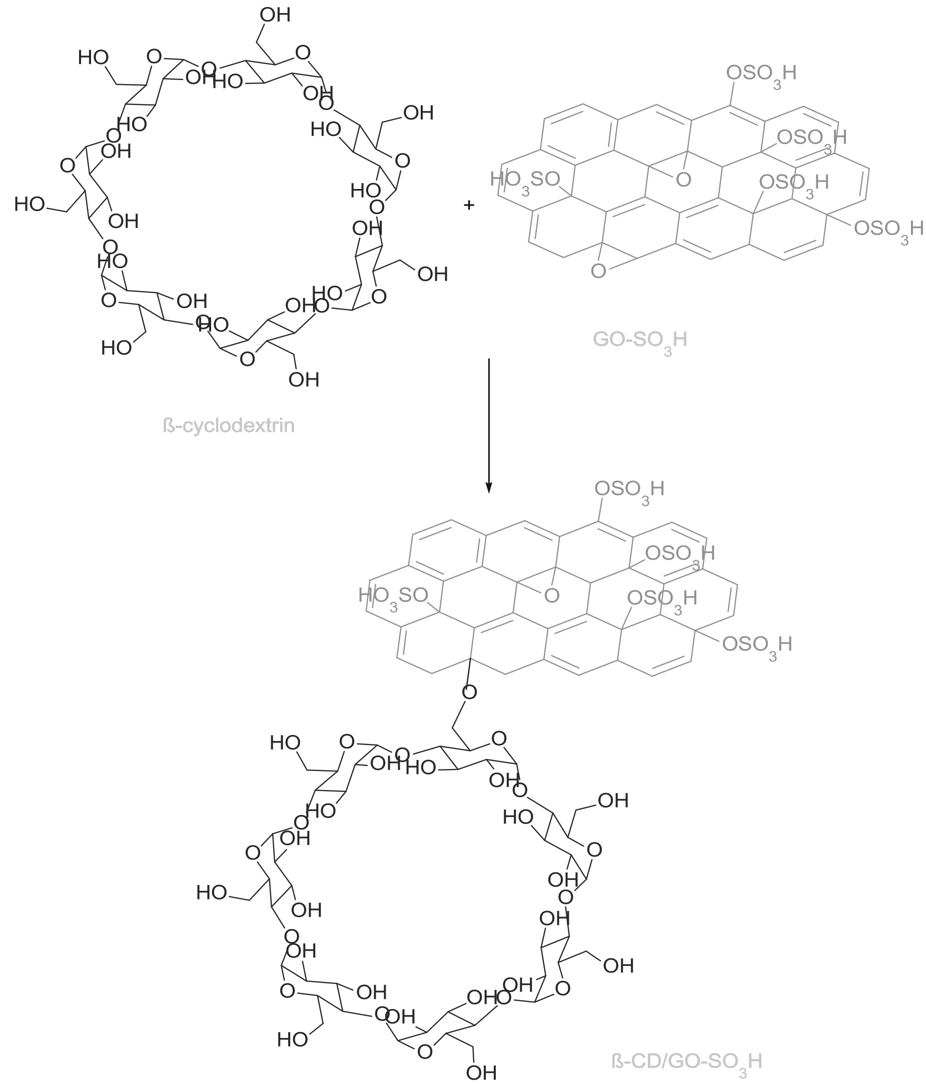
2.2 Serum sample preparation

Human blood serum samples were obtained from healthy volunteers. They were centrifuged at 4,000 rpm for 30 min at room temperature to remove serum proteins. Then, 1.2 mL acetonitrile was added to remove serum protein. After vortexing for 1 min, the mixture was centrifuged for 10 min at 6,000 rpm to remove the serum protein residues. Supernatant was taken carefully and appropriate volumes of this supernatant were transferred into the electrochemical cell and diluted up to the volume with the PBS.

2.3 Apparatus

Electrochemical measurements were carried out in a conventional three-electrode cell containing 0.1 M PBS pH 6.00 (which was employed as the running electrolyte throughout the work) powered by a Potentiostat/Galvanostat, an Autolab, and PGSTAT 302 N (Eco Chemie, Netherlands). Ag/AgCl and Pt wire were used as the reference and counter electrodes, respectively. The system was run by a PC through NOVA software. The working electrode was a glassy carbon electrode (GCE) (from Azar Electrode Co., Urumia, Iran) and β-CD/GO-SO_3H/GCE, exposing a geometric surface area of 0.0314 cm^2.

Scheme 1 Synthesis procedure of β-CD/GO-SO_3H



2.4 Synthesis of the β-CD/GO-SO_3H

At first, the GO-SO_3H was prepared according to our previous work [44]. Then, β-CD/GO-SO_3H was synthesized according to the literature [45]. Briefly, 20 mL of the homogeneous GO-SO_3H dispersion (0.5 mg/mL) was mixed with 20 mL of β-CD aqueous solution (80 mg) and 300 mL of ammonia solution. After being vigorously shaken for a 10 min, the vial was put in a water bath (60 °C) for 3.5 h. The stable black dispersion was obtained. The dispersion was filtered with a nylon membrane (0.22 mm) to obtain β-CD/GO-SO_3H hybrid that can be redispersed readily in water by ultrasonication (Power: 100 W; Frequency: 40 kHz) for 5 min (Scheme 1).

2.5 Characterization of β-CD/GO-SO_3H

The properties of β-CD/GO-SO_3H are highly related to their microstructures, their dispersity, and the morphology of β-CD. The presence of β-CD in our samples of hybrid was confirmed by SEM and TEM (Fig. 1). For recording TEM and SEM, 5 μL of 0.25 mg mL^{-1} β-CD/GO-SO_3H was carefully cast on the surface of the GCE which the shape of electrode was disk with a diameter of 2 mm. The added β-CD to GO-SO_3H can be seen as cavities that were spread on the surface of GO-SO_3H.

2.6 Preparation of the β-CD/GO-SO_3H/GCE

Prior to the modification, the GCE was polished with 1, 0.3, and 0.05 μm alumina slurry and rinsed thoroughly with double distilled water between each polishing step. Then, it was washed successively with 1:1 nitric acid, acetone, and double distilled water in an ultrasonic bath and dried in air. Lastly, 5 μL of 0.25 mg mL^{-1} β-CD/GO-SO_3H was carefully cast on the surface of the well-polished GCE and dried in room temperature (1 h). The β-CD/GO-SO_3H/GCE was thus obtained.

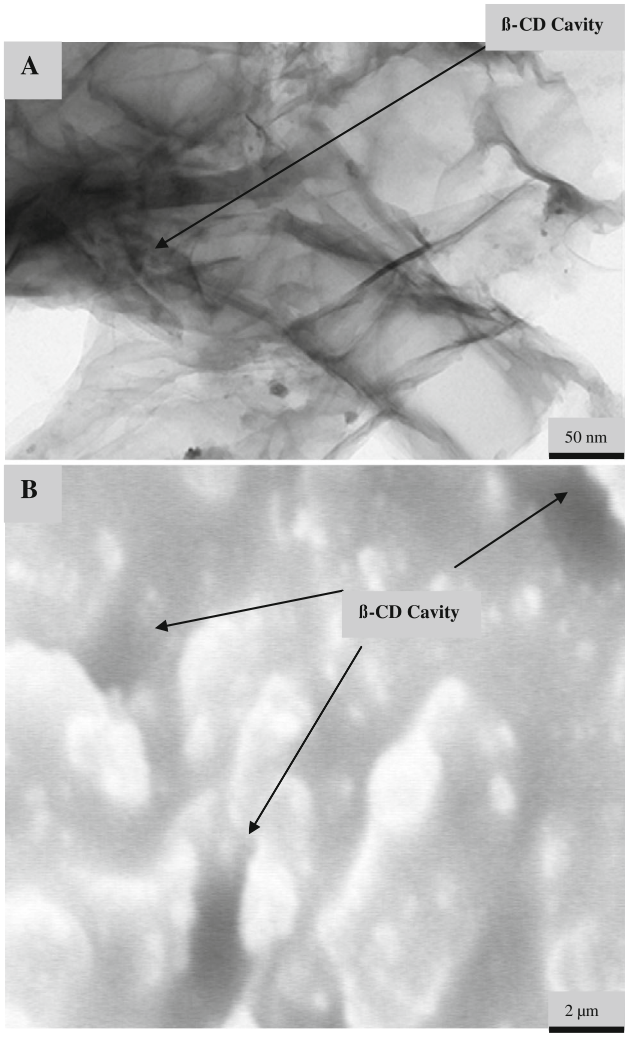


Fig. 1 TEM (A) and SEM (B) of β-CD/GO-SO_3H

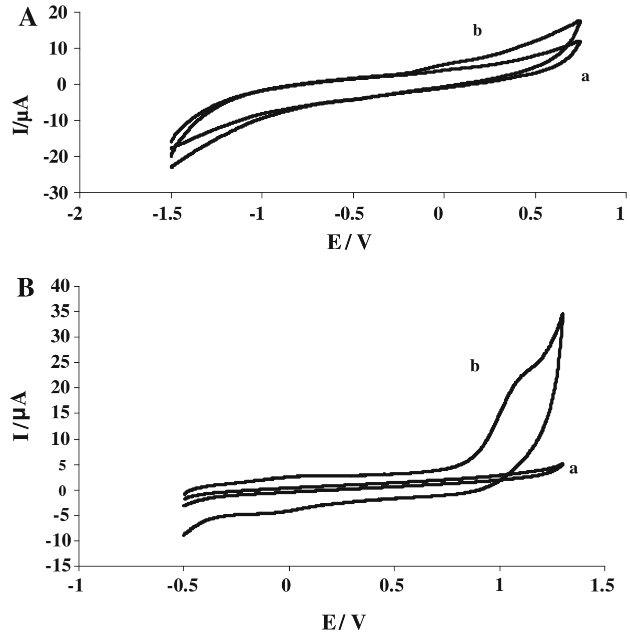


Fig. 2 CVs of bare GCE (**A**) and β-CD/GO-SO_3H/GCE (**B**) in solution without (*a*) and with 0.01 mM lisinopril (*b*). Supporting electrolyte: 0.1 M; PBS (pH 6.00); scan rate: 100 mV s^{-1}

3 Results and discussion

3.1 Electrochemical behaviors of lisinopril

The voltammograms of lisinopril at a bare GCE and β-CD/GO-SO_3H/GCE in PBS (pH 6.00) are shown in Fig. 2.

As seen in Fig. 2A any oxidation signal was not exhibited on the GCE. This indicated the electroinactivity of lisinopril on the GC surface. Typical cyclic voltammograms (CVs) of β-CD/GO-SO_3H/GCE in 0.1 M PBS are shown as Fig. 2B where potential sweep rate of 100 mVs^{-1} has been employed. In the absence of lisinopril, no peak appears at the β-CD/GO-SO_3H/GCE. While lisinopril exhibits one oxidation peak, located at 0.98 mV. It showed that no reduction peak was observed in the reverse scan, suggesting that the electrochemical reaction was a totally irreversible process. As can be seen, the anodic peak potential for the oxidation of lisinopril at β-CD/GO-SO_3H/GCE is about 0.98 V. The oxidation peak current value (I_p) of lisinopril was 23 μA. The data obtained clearly show that the combination of GO-SO_3H and β-CD definitely improve the characteristics of lisinopril oxidation. That might be related to the excellent property of β-CD/GO-SO_3H, such as high specific surface area and electrical conductivity. The role of β-CD was also important for promoting the electrochemical oxidation of lisinopril. So, β-CD/GO-SO_3H could be substituted for the oxidation of lisinopril.

3.2 Effect of pH value

The effect of solution pH on the electrochemical response of 0.01 mM lisinopril at β-CD/GO-SO_3H/GCE was investigated with PBS solution in the pH range of 2.00–11.00 by CV. As shown in Fig. 3A, it can be realized that the anodic peak currents of lisinopril are increased slightly when there is an increase in the pH solution until 6.00. This can be attributed to the deprotonization of lisinopril. When lisinopril changed from neutral to cation form its electrostatic accumulation on the electrode surface increased. Therefore, PBS solution of pH 6.00 was chosen for the subsequent analytical experiments.

The peak potential was closely dependent on the pH of the solution. It was found that the values of peak potential shifted to negative values with the increase of pH (as shown in Fig. 3B). The peak potential (E_p) moved in negative direction with pH rising and they showed such relationship as $E_p = -0.0624$ pH $+1.1255$ ($R^2 = 0.9932$).

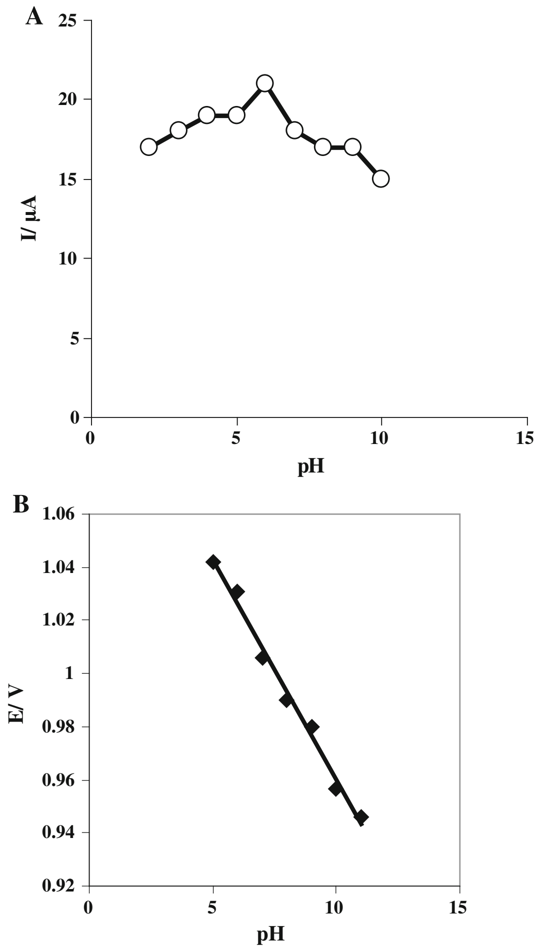


Fig. 3 Influence of pH on the oxidation peak current (**A**) and Potential (**B**) of 0.01 mM lisinopril

The slope of -62.4 mV pH^{-1} demonstrated that the numbers of electron and proton transferred in the electrochemical reaction of lisinopril were equal.

3.3 Effect of scan rate

Useful information involving electrochemical mechanism usually can be acquired from the relationship between peak current and scan rate. Therefore, the electrochemical behaviors of lisinopril at different scan rates were investigated on the surface of β-CD/GO-SO_3H/GCE by CV. A linear relationship was obtained between the peak current and the scan rate in the range of 10–500 mV s^{-1}, which revealed that the oxidation of lisinopril was a diffusion-controlled step (Fig. 4).

The peak potential shifted to positive values with the increasing scan rates. The linear relation between peak potential and logarithm of scan rate can be expressed as $E_p = 0.0349 \ln v + 0.9877$ ($R^2 = 9963$). As for an irreversible electrode process, according to Laviron [46], E_p is defined by the following equation:

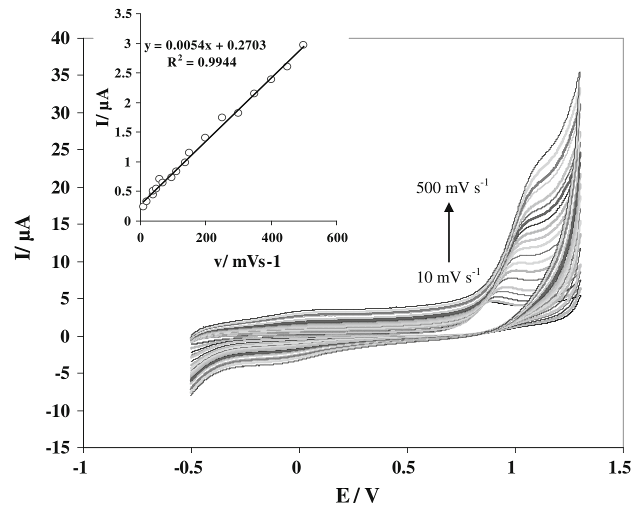


Fig. 4 Cyclic voltammograms of β-CD/GO-SO_3H/GCE in the presence of 0.01 mM lisinopril in different scan rates (from inner to outer): 10, 20, 30, 40, 50, 60, 70, 90, 110, 130, 150, 200, 250, 300, 350, 400, 450, and 500 mV s^{-1}, respectively. *Inset* Peak current versus scan rate

$$E_p = E^0 + \frac{RT}{(1-\alpha)nF} \ln v, \tag{1}$$

where E_p is the peak potential (V *vs.* Ag/AgCl), E^0 is the formal potential (V *vs.* Ag/AgCl), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the temperature (K), α is the charge transfer coefficient for the oxidation step, n is the number of electrons involved in the rate determining step, and F is the Faraday constant (96,485 C mol^{-1}). According to Bard and Faulkner [47], for a totally irreversible wave, E_p is a function of scan rate, shifting (for an oxidation) in a positive direction by an amount $1.15RT/\alpha F$ (or 30/α mV at 25 °C) for each ten-fold increase in v. So, from this we got the value of α to be 0.30. The number of electron (n) transferred in the electrooxidation of lisinopril was calculated to be 0.97 (approximately equal to 1).

Literature information reveals that the increased anodic signal may also be a result of its inclusion into the hydrophobic cavity of β-CD [48]. This inclusion may result in a sort of pre-concentration of the drug at the electrode surface, which will govern the kinetics of its charge transfer process. In the case of lisinopril, the obtained slight increase in the redox peak current can be due to a partial inclusion into the β-CD.

Figure 5 shows that upon increasing lisinopril concentration its irreversible oxidation develops in the region of the electrochemical formation of oxidation product. Any increase in the concentration of lisinopril causes a proportional and nearly linear enhancement of the anodic wave. It is worthwhile to emphasize that the anodic formation of oxidation product is an irreversible process.

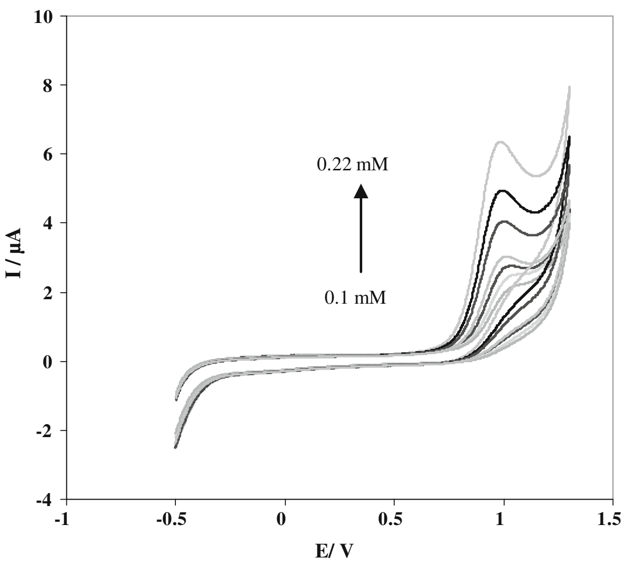


Fig. 5 Cyclic voltammograms for 0.1, 0.12, 0.14, 0.16, 0.18, 0.2, and 0.22 mM of lisinopril

3.4 Chronocoulometry

The electrochemically effective surface areas (A) of GCE and CD/GO-SO_3H/GCE were investigated by chronocoulometry using 0.1 mM $K_3[Fe(CN)_6]$ as a model complex (the diffusion coefficient of $K_3[Fe(CN)_6]$ in 1 M KCl is 7.6×10^{-6} cm^2 s^{-1} [49]) based on Anson equation:

$$Q(t) = \frac{2nFACt^{1/2}D^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads}, \tag{2}$$

where C is the substrate concentration, D is the diffusion coefficient, n is the electron transfer number, Q_{dl} is double layer charge which could be eliminated by background subtraction, and Q_{ads} is the Faradic charge. Other symbols have their usual meanings. Based on the slopes of the curves of Q versus $t^{1/2}$ (Fig. 6A), one can calculated effective surface areas to be 0.097 and 0.309 cm^2 for GCE and β-CD/GO-SO_3H/GCE, respectively. These results indicate that β-CD/GO-SO_3H can significantly increase the reaction surface area of electrodes and enhance the current of the charge transfer reaction between the electrode and solution species for lower electrode polarization.

The diffusion coefficient (D) of lisinopril at β-CD/GO-SO_3H/GCE can also be determined by chronocoulometry based on Eq. (2). As shown in Fig. 6B, a linear relationship between Q and $t^{1/2}$ can be obtained after point-by-point background subtraction, and the regression can be expressed as $Q = 1.017 \times 10^{-5}$ $t^{1/2} + 6.634 \times 10^{-5}$(C $s^{1/2}$, $r = 0.9944$). Based on the slope of 1.017×10^{-5} C $s^{-1/2}$, it is calculated that $D = 4.8 \times 10^{-5}$ cm^2 s^{-1}.

Figure 7 shows the DPV of 1 μM lisinopril at β-CD/GCE, GO-SO_3H-GCE, and β-CD/GO-SO_3H-GCE. The current response of lisinopril at the β-CD/GO-SO_3H-GCE is much higher than that at the β-CD/GCE and GO-SO_3H-GCE, indicating that β-CD/GO-SO_3H-GCE possesses remarkable enhancement effects on the oxidation of lisinopril. It is noteworthy that the present response of lisinopril was dramatically improved when β-CD was introduced to the surface of GO-GCE. This can attribute to hydrogen bonding between the β-CD and lisinopril. This leads to a greater amount of lisinopril accumulation on the surface of β-CD/GO-SO_3H-GCE. Therefore, for these three modified electrodes, the value of the oxidation peak current follows the order of I_p [β-CD/GO-SO_3H-GCE] > I_p [GO-SO_3H-GCE] > I_p [β-CD/GCE].

3.5 Calibration curve

In order to develop a voltammetric method for determining of lisinopril, we selected the DPV mode, because the peaks are sharper and better defined at lower concentration of lisinopril than those obtained by CV, with a lower background current, resulting in improved resolution. According to the obtained results, it was possible to apply this technique to the quantitative analysis of lisinopril. The PBS of pH 6.00 was selected as the supporting electrolyte for the quantification of lisinopril as it gave maximum peak current at pH 6.00. The peak at about 0.98 V was considered for the analysis of DPVs obtained with increasing amounts of lisinopril showed that the peak current increased linearly with increasing concentration, as shown in Fig. 8.

Using the optimum conditions described above, linear calibration curves were obtained for lisinopril in the range of 0.21–190.4 μM. The linear equation was $I_p(A) = 0.0093C$ (μM) + 0.3852 ($R^2 = 0.9927$). The detection limit was estimated to be 0.11 μM (S/N = 3). The comparison of β-CD/GO-SO_3H/GCE with other electrodes for the lisinopril determination is listed in Table 1.

It can be seen that the β-CD/GO-SO_3H/GCE offered reasonable linear range for lisinopril detection and the detection limit was lower than some of previous reports. These results indicated that β-CD/GO-SO_3H/GCE is an appropriate platform for the determination of lisinopril. On the other word, the prepared electrode shows voltammetric responses with low detection limit and wide linear range for lisinopril in optimal conditions, which makes it suitable for determination of this drug. It is found that, by incorporating β-CD as cavity entrapper in GO, a novel strategy for developing an efficient and robust electrochemical sensing platform was established. The electrochemical sensor showed high sensitivity and simplicity for detection of lisinopril.

3.6 Reproducibility and stability

Another advantage of the proposed modified electrode was that the resulting modified electrode showed good long-term stability. Stability of the proposed electrode was tested by

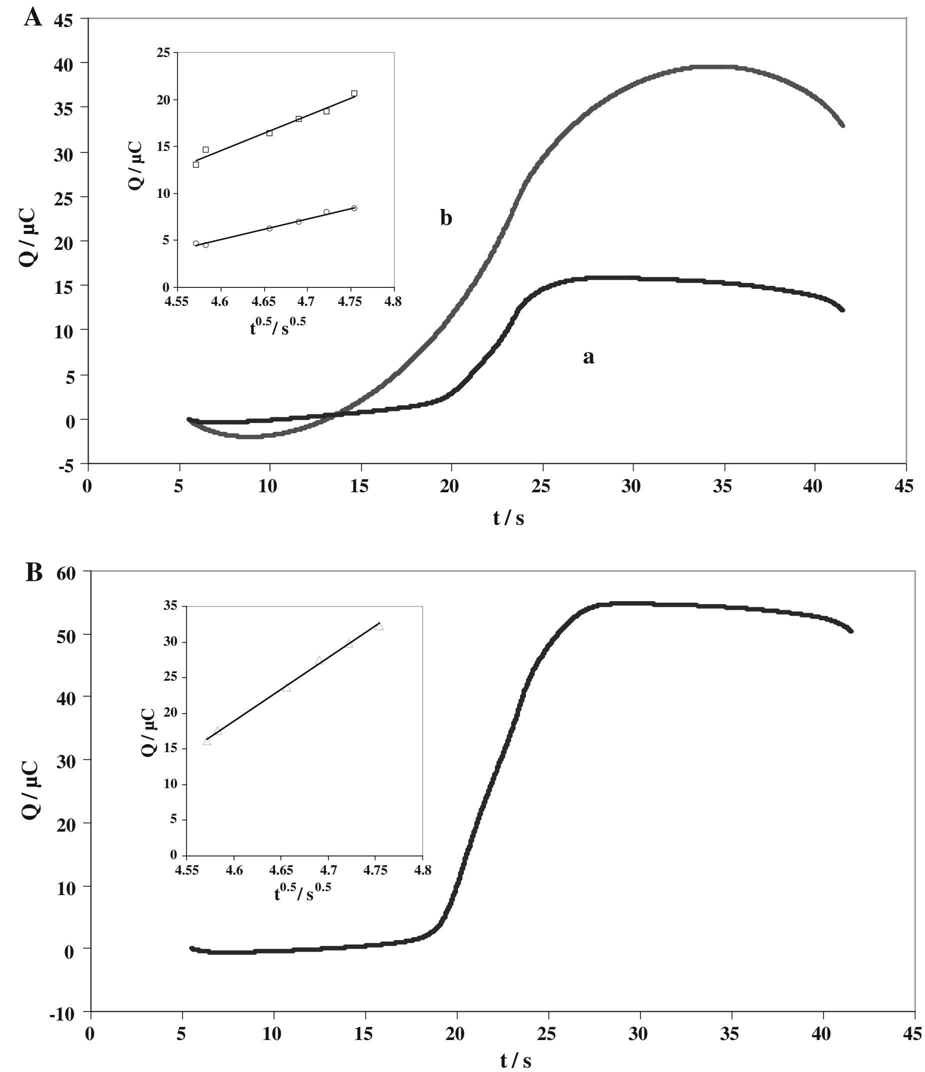


Fig. 6 **A** Plot of Q-t curve of GCE (*a*) and β-CD/GO-SO_3H/GCE (*b*) in 0.1 mM $K_3[Fe(CN)_6]$ containing 1 M KCl. *Inset* Plot of Q-$t^{1/2}$ curve on GCE and β-CD/GO-SO_3H/GCE. (**B**) Plot of Q-t curve of 0.01 mM lisinopril at β-CD/GO-SO_3H/GCE after background subtraction. *Inset* Plot of Q-t $^{1/2}$ curve

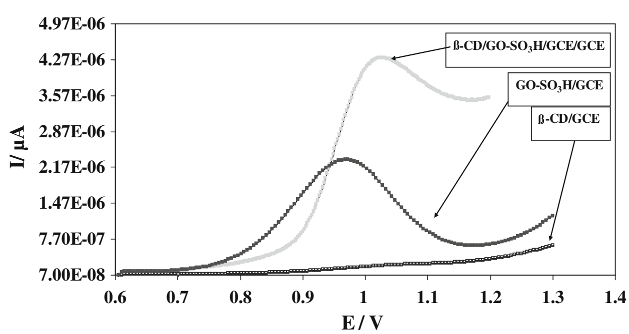


Fig. 7 Differential-pulse voltammograms of 10 μM lisinopril at bare β-CD/GCE, GO-SO_3H-GCE, and β-CD/GO-SO_3H-GCE

measuring the decrease in voltammetric current during repetitive DPV measurements of lisinopril with β-CD/GO-SO_3H/GCE stored in solution or air. For example, this electrode, within 24 h, is used for the determination of 10 μM lisinopril in buffer solutions. Obtained results show that this electrode has remarkable stability without significant change in the voltammetric currents. When the electrode was stored in the atmosphere, the current response remained almost unchanged for about 1 month (exactly 26 days). RSD of repeated peak currents was (4.7 %). The high stability of the β-CD/GO-SO_3H/GCE could be related to the strong affinity of β-CD for GO-SO_3H and the low solubility of the β-CD/GO-SO_3H in water. To check the inter-electrode reproducibility of the modified electrode, four modified electrodes were tested simultaneously by recording DPVs in buffer solution, containing 10 μM of lisinopril. The relative standard deviation was 4.4 %. Therefore, β-CD/GO-SO_3H/GCE imparts a suitable stability onto DPVs measurements of lisinopril.

3.7 Analytical application

The high sensitivity of the proposed method and β-CD cavities allows the determination of lisinopril in spiked human serum

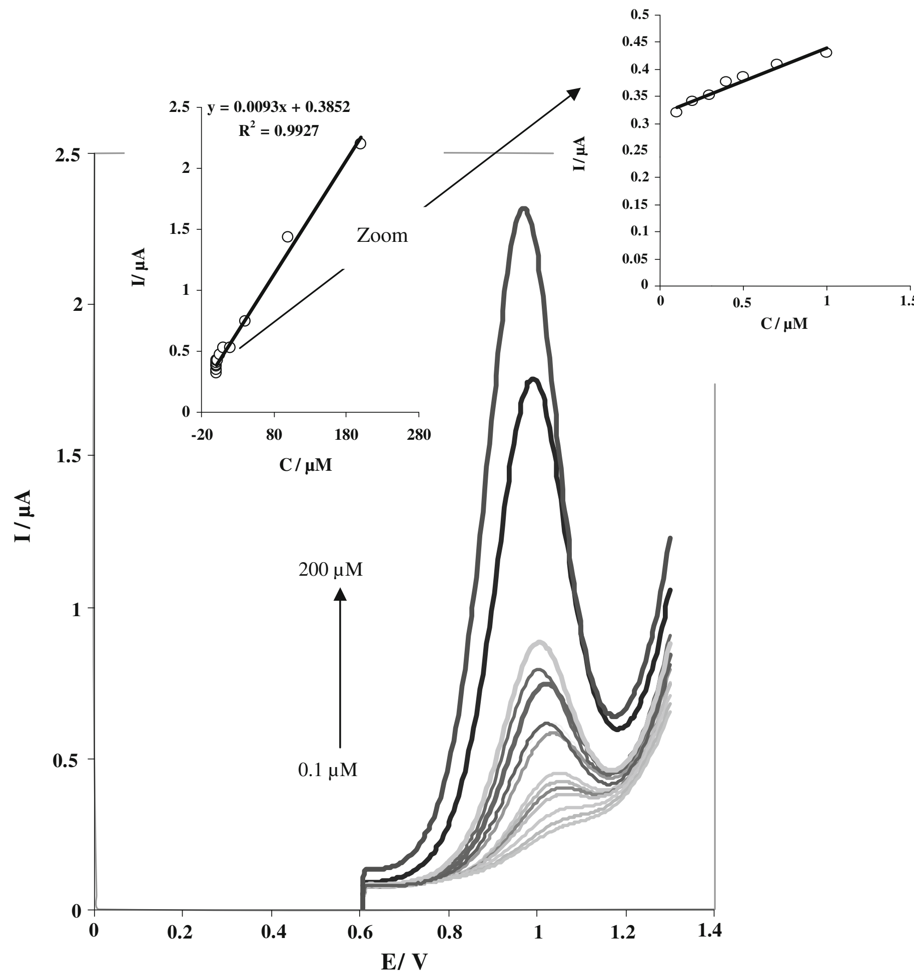


Fig. 8 Differential pulse voltammograms of β-CD/GO-SO_3H/GCE in different concentrations of lisinopril solutions (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 1, 2, 5, 10, 20, 40, 100, and 200 μM). *Inset* calibration curve

Table 1 Performance comparison of the fabricated electrode for lisinopril with other electrodes

Electrode	Method	Linear range	LOD (μM)	Ref.
Au	Amperometric	0.026–2.2 mM	272	[50]
PVC	Potentiometry	0.1 μM–0.1 mM	0.794	[16]
PVC-based coated wire electrode		1 μM–1 mM	0.425	
Tecoflex-graphite		1 μM–0.1 mM	0.498	
β-CD/GO-SO_3H/GCE	DPV	0.21–190.4 μM	0.11	This work

samples (Table 2). The recovery of the analytes was measured by spiked drug into diluted serum samples. The DPVs were recorded after the serum was spiked with various amounts of the lisinopril within the working concentration range. Recoveries were found to lie in range of 97.1–105.0 %. Good recoveries of lisinopril were achieved from this method, meaning that application of proposed sensor to the analysis of lisinopril in biological fluids could be easily assessed.

Table 2 Determination of lisinopril in human serum by β-CD/GO-SO_3H/GCE

Sample	Added (μM)	Found (μM)	Recovery (%)
Human serum	0	Not detected	–
	10	10.5	105.0
	50	52.0	104.0
	100	98.1	97.1

4 Conclusions

β-CD/GO-SO_3H can adsorb lisinopril and promote its electron transfer, thus β-CD/GO-SO_3H/GCE provides higher electroactive surface area and lower charge transfer resistance compared with GCE. The electrochemical process is irreversible and presents the feature of an adsorption-controlled system. The peak current and lisinopril concentration show a linear relationship in a wide range. The electrode exhibits good repeatability and stability. This proposed method could be applied to the determination of lisinopril in medicines. Lisinopril can produce a more sensitive anodic peak at the β-CD/GO-SO_3H/GCE.

Acknowledgments This is a report of a database from the thesis entitled "Development of sensitive, routine and reliable methods for determination of cardiovascular drugs in biological samples" registered in Drug Applied Research Center. We gratefully acknowledge the financial support of this work by the Drug Applied Research Center, Tabriz University of Medical Sciences.

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